Activating Mg acceptors in AlN by oxygen: first principles calculations

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Abstract

First principles calculations based on density functional theory (DFT) are performed to study the electronic properties of Mg acceptors in AlN at the presence of oxygen. It is found that Mg and O tend to form complexes like Mg-O, Mg$_2$-O, Mg$_3$-O and Mg$_4$-O which have activation energies about 0.23 eV lower than that of Mg (except of the passive Mg-O). The lower activation energies originate from the extra states over valence band top of AlN induced by the passive Mg-O. By comparing to the well-established case of GaN, it is possible to fabricate Mg and O codoped AlN without MgO precipitate. These results suggest the possibility of achieving higher hole concentration in AlN by Mg and O codoping.

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Ultraviolet light-emitting diodes (LEDs) with wavelengths less than 300 nm are of considerable technological significance. They are potential alternatives to the existing gas lasers and mercury lamps in applications such as disinfection, air and water purification and biomedicine where the latter encounter difficulties due to their high operating voltages, low efficiency, large size and toxicities.[1] They also promise high density optical data storage and high-resolution photolithography.[2] Wide gap semiconductors, diamond (E_g=5.5 eV) and AlN (E_g=6.2 eV) are the two most studied materials for such LEDs and AlN is particularly favored due to its direct gap band structure and subsequent high light-emission efficiency. Diamond as well as AlN based LEDs have been fabricated recently.[3, 4] However, in view of their low efficiency and high operating voltages, further developments are still required to improve these two LEDs to the point where they can be used as devices.[5]

Fabrication of a homo-structured LED requires both p- and n-type doping of a semiconductor. Unfortunately, the asymmetry dopability of wide gap semiconductors makes the fabrication of LEDs very difficult. The asymmetry dopability means that a wide gap semiconductor can be either p- or n-type doped,but not both.[6] AlN can be easily n-type doped with Si. However, p-type AlN is of great challenge. The most promising acceptor for AlN is Mg. Yet, the activation energy (E_A) of the Mg acceptor in AlN is 0.5 eV.[7, 8] As the ratio of carrier concentration to impurity concentration follows $\exp(-E_A/k_B T)$, where k_B is the Boltzmann constant and T is the temperature, only a very small fraction $\sim 10^{-8}$ of Mg impurities is activated at room temperature. Since the upper limit of Mg concentration in AlN is 2×$\sim 10^{20}$cm^{-3},[4], the corresponding hole concentration for Mg-doped AlN would not exceed $\sim 10^{12}$cm^{-3}. This concentration, however, is still well below that for device applications (which requires a hole concentration at least 10^{17}cm^{-3}).

Recently, codoping has been proposed and applied to overcome difficulties in p-type doping in some wide gap semiconductors such as GaN and ZnO.[9] Significant improvements in hole concentrations have been achieved in these two semiconductors. In this approach, p-type dopants (D) are incorporated into the semiconductor along with a small amount of reactive n-type impurities as codopants (CD). Then in the host semiconductors, complexes like D-CD,D_2-CD, D_3-CD and D_4-CD will form and more often they have lower ionization energies than that of mono-dopant D(expect for D-CD which is passive). Thus the hole concentration may be greatly enhanced. By this approach, the hole concentration in ZnO was improved from $\sim 10^{13}$cm^{-3} in N-mono-doped ZnO to $\sim 10^{17}$cm^{-3} or ever higher in (Al,Ga or

In)-N codoped ZnO.[10, 11, 12] Codoping also enhanced the hole concentration in Mg doped GaN. The conductivity of Mg doped GaN could be significantly enhanced by annealing in an environment with oxygen.[13] This enhancement in conductivity was attributed to the decreased activation of Mg acceptors due to the inclusion of oxygen and a corresponding order of magnitude increase of hole concentration(from $\sim 10^{17} \text{cm}^{-3}$ to $\sim 10^{18} \text{cm}^{-3}$).[14]

It is therefore reasonable to believe that the hole concentration of Mg-doped AlN can be improved using a similar approach. In this letter, we investigate the effect of atomic oxygen on the activation energy of Mg acceptors in AlN by first principles electronic calculations based on density functional theory (DFT). We first study the possibility of the formation of Mg_n-O (here n ranges from 1 to 4; atomic O occupies N site and atomic Mg the neighboring Al site, respectively) complexes in AlN. All these complexes under study are assumed to be electrically neutral unless otherwise stated. This is reasonable since even at an activation energy as low as 0.20 eV, only a small portion ($\sim 10^{-4}$) of the acceptors are in charged state. Then the activation energies of *complex acceptor* Mg_n-O is calculated. To explain the results obtained, the density of states (DOS) are given . Most of the calculations are done using a 3×3×2 supercell constructed from AlN unit cell using the plane-wave DFT code VASP.[15, 16] The lattice constants of the supercell are kept fixed to avoid effects from spurious volume expansion. The Γ-centered 4×4×4 k-mesh is used for irreducible Brillouin zone sampling. The ion-electron interaction is described by Vanderbilt ultrasoft pseudopotentials[17]with local density approximation (LDA) for the exchange-correlation potential. The electron wave function is expanded in plane waves with a cutoff energy of 400 eV. These parameters ensure a convergence better than 1 meV for the total energy. In all the doped supercells, atomic coordinates are fully relaxed using the conjugate-gradient algorithm[18] until the maximum force on a single atom is less than 0.03 eV/Å.

For AlN in wurtzite structure the calculated lattice constants are 3.08 Å for a and 4.94 Å for c with the internal parameter being 0.382, in good agreement with experimental values. Based on this the 3×3×2 supercell ($Al_{36}N_{36}$) is constructed. Previous calculations on formation energies have shown that O occupies N site in AlN as a deep donor[19, 20] and consequently in our supercell one N atom is replaced by an O atom. This O donor may act as an attraction center to single Mg atom and form complexes such as Mg-O, Mg_2-O, Mg_3-O and Mg_4-O with Mg atoms occupying the nearest Al sites to O and without destroying the lattice structure. To study whether single Mg atom will bind to Mg_n-O (n=0,1, 2 and 3,

3

respectively) complexes, we define the *binding energy* as the energy required to form the Mg_{n+1}-O complex from well separated Mg dopant and Mg_n-O complex:

$$\Delta^{(n)} = E(Al_{36-n-1}Mg_{n+1}N_{35}O) + E(Al_{36}N_{36})$$

$$-E(Al_{35}Mg_1N_{36}) - E(Al_{36-n}Mg_nN_{35}O) \qquad (1)$$

where E is the total energy of the system indicated in parentheses. A negative $\Delta^{(n+1)}$ suggests that the Mg_{n+1}-O complex is energetically favorable and stable while a positive $\Delta^{(n)}$ suggests that Mg_{n+1}-O cannot form. The calculated $\Delta^{(n)}$ are summarized in Table I. As can be seen, single Mg atom will bind to single O atom for a large energy decrease of 5.304 eV. This large energy decrease can be attributed to the passivation of the extra electron of O by Mg. The energy decrease from single Mg atom binding to Mg-O complex is 0.626 eV, suggesting that Mg_2-O complex will form provided the amount of Mg exceeds that of O. If there are still extra Mg acceptors available then Mg_3-O will form with an energy decrease of 0.412 eV . Formation of Mg_4-O from single Mg atom and Mg_3-O is less likely although also exothermic due to a much smaller energy decrease of 0.157 eV. The binding of single Mg atom to the O atom in Mg_n-O complexes can be attributed to the larger electronegativity of O than that of N.

Now we calculate the activation energy of the Mg_2-O complex which is the most probable complex when the concentration ration between Mg and O is around 2. The method proposed by Van de Walle is applied for the activation calculation:[21]

$$E_A = E_{tot}[D^-] - E_{tot}[D^0] - E_v - \Delta V[D] + E_{corr} \qquad (2)$$

where E_A is the activation energy of the defect (donor) D. $E_{tot}[D^-]$ and $E_{tot}[D^0]$ are the total energies of the supercell with defect in charged (-) and neutral (0) state, respectively. E_v is the valence band maximum of the bulk semiconductor; $\Delta V[D]$ is a correction term to align the reference potential in the charged defected supercell with that of the bulk and it is derived from the electrostatic potential difference between the bulk and that of the defected supercell far away from defect site. Using a 5×5×3 supercell a value of -0.15 eV is calculated for both $\Delta V[Mg]$ and $\Delta V[Mg_2 - O]$. Calculation obtained using a larger 6×6×4 supercell gives out does not result in any significant change in these values. E_{corr} is a correction term for the use of Γ-included k-mesh sampling for the hexagonal lattice. In practice this is derived from the energy difference between the highest occupied level at

Γ-point and other special k-points (averaged) in the supercell containing the neutral defect D. The calculated E_{corr} is 0.26 eV for supercell containing only Mg defect and 0.03 eV for the supercell containing Mg$_2$-O complex. The calculated ionization of single Mg acceptor in AlN is 0.40 eV which is in agreement with previous DFT-LDA calculation ($\sim$ 0.45 eV [22]) and experiments ($\sim$ 0.5 eV[7, 8]). For the Mg$_2$-O complex, the calculated E_a is only 0.17 eV, 0.23 eV lower than that of single Mg acceptor. If we apply this decrease to the experimental value, then following $\exp(-E_A/k_B T)$, the hole concentration can be increased by at least a factor of 10^3. This is a significant improvement, although the total carrier concentration is still below the value desired. Other clusters Mg$_3$-O and Mg$_4$-O have very close activation energies to that of Mg$_2$-O. Thus incorporation of some amount of oxygen into Mg-doped AlN can improve the hole concentration.

The decreased activation energy in the Mg acceptor after attaching to O-Mg complex can be understood from the density of states of the defected supercell as shown in Figure. 1. Although O-Mg complex is passive and cannot accept the host valence electrons, it induces extra fully occupied states right on the valence band maximum (VBM) as indicated by the DOS curve of AlN supercell containing Mg-O complex. In the Mg-O complex some electrons have higher energy than that of the host valence electrons. Thus Mg atoms binding to this complex may be activated by electrons from these *complex states* rather than from the host states. So the activation energy is decreased.

However, for such a codoping the growth condition should be chosen carefully. This is because under thermal equilibrium the formation energies of Mg$_n$O complexes will be rather high. The formation energy is given by:

$$E^f[D(q)] = E^{tot}[D(q)] - E^{tot}[bulk] - \Sigma_i n_i \mu_i$$
$$+q(E_f + E_v) \tag{3}$$

where the $E^{tot}_{defect}(q)$ is the total energy of the supercell containing the defect, $E^{tot}(bulk)$ is the total energy of a similar supercell containing the pure crystal, n_i is the number of atoms that is involved in the formation of the defect with μ_i being the corresponding chemical potentials. E_f is the Fermi energy which is set to zero at the valence-band maximum E_v. The chemical potentials depend on the experimental growth conditions, which can be either Al-rich or N-rich. Formation of AlN crystal under thermal equilibrium requires $\mu_{Al}+\mu_N=\mu_{Al}[bulk]+\frac{1}{2}\mu_N[N_2]+\Delta H[AlN]$, where $\Delta H(AlN)$ is the formation enthalpy of AlN.

In the N-rich condition which is preferred for incorporating Mg at Al sites, the upper limit of μ_N is given by $\mu_N[N_2]$, i.e., the energy of N in a N_2 molecular. $\Delta H[AlN]$ is calculated to be -3.58 eV. The formation energy of Mg on Al site at neutral state is $E^f[Mg_{Al}(0)]$=1.76 eV with the solubility limit imposed by $3\mu_{Mg}+2\mu_N=3\mu_{Mg}[bulk]+2\mu_N[N_2]+ \Delta H(Mg_3N_2)$. However, if O_2 is present in N_2 flux, to avoid the formation of MgO precipitate the upper limit of μ_{Mg} follows:

$$\mu_{Mg} + \mu_O = \mu_{Mg}[bulk] + \mu_O[O_2] + \Delta H(MgO)$$

where $\Delta H(MgO)$=-6.69 eV from our calculation. Under this constrain the formation energies of Mgn-O complexes become rather high. The formation energy of Mg$_2$-O complex is calculated to be 4.81 eV, suggesting an ignorable concentration of Mg$_2$-O complex in AlN in a growth process which is close to thermal equilibrium. However, this solubility limit can be overcome by proper growth conditions, i.e. high growth temperature and high growth rate. For example, in the doping of GaN with Mg as acceptors by gas-source epitaxy method, the inclusion of oxygen did not result in the MgO precipitate in GaN while improved the hole concentration significantly.[14, 23] By calculation, the formation energy of Mg$_2$-O complex in GaN is 6.31 eV, significantly higher than that of AlN. Thus in AlN, the solubility limit problem is less severe. This suggests the possibility of Mg and O codoping in AlN without MgO precipitates.

To summarize, we have studied the electronic properties of Mg acceptors in AlN at the presence of oxygen by first principles calculations. Our calculations suggest the formation of of Mg$_n$-O complexes and their lower activation energies compared to Mg. Compared to the well established case of GaN, the MgO precipitate problem can be overcome. Our results suggest that the hole concentration in AlN:Mg can be greatly enhanced by oxygen codoping.

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TABLE I: *Binding energy* for single Mg acceptor to Mg_n-O complex . Unit: eV

n	0	1	2	3
$\Delta^{(n)}$	-5.304	-0.626	-0.412	-0.157

FIG. 1: Total DOS of supercells with pure AlN [curve marked by AlN] and AlN containing one passive Mg-O complex [curve marked by AlN(Mg-O)]. The bold arrow indicates the extra states on the top of the VBM of the pure AlN. The Fermi level of the pure AlN is indicated by the vertical dashed line.